

Thermal Stability and Compression Strength of Rigid Polyurethane/Kenaf Fibre Biocomposite Foam

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Rigid palm oil-based polyurethane/kenaf fibre biocomposite foams were prepared at various amounts of kenaf fibre (i.e. 2.5, 5.0, 7.5, 10.0 and 12.5 pphp). Effects of kenaf fibre (KF) loadings on thermal stabilities and compressive strength were investigated. The peaks detected by Fourier transform infrared (FTIR) at 3,310 cm^{-1} (OH stretching), 1,533 cm^{-1} (NH bending) and 1,510 cm^{-1} (CN stretching) had proved the formation of urethane linkages in the system. Results from thermogravimetric analysis (TGA) showed that the thermal stabilities of biocomposite foams were higher than that of control PU foam. Higher KF contents resulted in agglomeration of which reduced the rate of heat transfer throughout the system. The presence of intra-hydrogen bonds in agglomerated KF caused more heat needs to break the bonds, thus increasing the thermal stabilities. Consequently, the agglomeration of KF created stress concentration, which reduced the compression strength of the foams with respect to the control PU foam. The presence of intra-hydrogen bonding in PU chains had surpassed the agglomeration effect, thus causing just a small reduction percentage. The foams have potentials to be used in non-load bearing applications such as insulators and wall panels.

1. Introduction

Polyurethane (PU) foam accounts for the largest global market at about 53 % compared to other polymeric foams (Chuayjuljit et al., 2010) and almost 67 % of the global PU consumptions in 2016 is for the making of foam (Gama et al., 2018). It has a remarkably broad range of applications from furniture, bedding, footwear, insulation panel, packaging and aircraft to automotive parts (Shan et al., 2012). PU foam is made by reacting diisocyanates with polyols components. The issues on environmental impact and sustainability have driven the development of PU foams from vegetable oil-based polyols (Prociak et al., 2012). Largely, petrochemical-based polyols such as polyethylene glycol (PEG) can be totally replaced (Tanaka et al., 2008) or mixed (Nasir et al., 2016) with vegetable oils-based polyols such as soybean oil and palm oil to produce PU foams. A drawback, PU vegetable oil-based polyols have low thermal stability and moderate mechanical properties due to the nature of the process to produce the polyols (Zlatanić et al., 2004). A process such as transesterification introduces hydroxyl group to the fatty acid chains of the vegetable oil but inevitably, this reaction leads to a decrease in the molecular weight and viscosity (Petrović, 2008). A common practice to enhance these properties is by adding fillers into PU matrices such as nanoclay (Liang and Shi, 2011), halloysite (Alis et al., 2019) and natural fibres (Mohd Soberi et al., 2017).

The utilization of natural fibres as fillers has attracted many researchers due to their toughnesses, less abrasive, more flexible, and biodegradabilities (Rowell et al., 1997). Silva et al. (2010) had found that by incorporating wood fibres into PU foam had improved the cell size. The presence of wood fibres had increased the viscosity in the system, which influenced the PU foam expansion and density. Badri et al. (2005) had added different sizes of empty fruit bunch (EFB) fibres into the palm kernel oil-based polyol PU foam. The compression strength of the composite foams with the smallest fibre size (45-56 μm) had increased with increasing fibres contents. Subramaniyan et al. (2013) had prepared PU foams filled with kenaf fibre:recycled tire rubber at 1:1 ratio. The compression strength and the modulus reached their maximum value at 6 % filler

loading. Further increase the filler content had weakened the cellular structure and led to the lower compression stress and compression modulus of PU foams. Across these studies, no details study had been reported on the effect of natural fibre on the thermal stability and compressive strength from a molecular level or bonding point of view.

In this paper, palm kernel oil-based polyol (PO-p) was reacted with polymeric 4, 4 – diphenylmethane diisocyanate (p-MDI) in the presence of silicone surfactant as a foam stabilizer and distilled water as a blowing agent to produce rigid PU foam. Kenaf bast fibre (KF) with the size of 150-300 μm was selected as a filler as it exhibits good mechanical behaviour, due to higher cellulosic content of the outer bast fibre i.e. 25-40 % (Saad and Kamal, 2013). However, to improve the interfacial adhesion between the fibre and the PU matrix, KF was treated with sodium hydroxide to reduce the hydrophilic property of the fibre, thus significantly improving the wettability of fibre with a polymer matrix (Majid et al., 2018).

2. Experimental section

2.1 Materials

Polymeric diphenylmethane 4,4'-diisocyanate (p-MDI) was supplied by Merck Sdn. Bhd, palm kernel oil-based polyol (PO-p) was obtained from Maskimi Polyol Sdn. Bhd., silicone surfactant (Tegostab B-8404) was purchased from Goldschmidt Chemical Corporation and the kenaf fibre was supplied by Everise Crimson (M) Sdn. Bhd. The size of KF used was 150-300 μm . Distilled water was used as a blowing agent. All the chemicals were used without further purification.

2.2 Preparation of Rigid PU/KF Biocomposite Foam

The PU composite foam-filled with KF was prepared via direct mixing at the ratio of 1:1 of NCO:OH. KF was treated with 5 wt% sodium hydroxide by following the method used by Low et al. (2018). A pre-mixture solution consists of silicone, PO-p, treated KF and distilled water were stirred at 1,500 rpm for 2 min using a mechanical stirrer to form a homogeneous solution. Then, p-MDI was added into the pre-mixture with continuous stirring for about 45 s before poured into a closed stainless-steel mould for creaming and self-raising process. The foam was left at room temperature for two days. The foam was conditioned at room temperature for a week prior to testing and characterizations. The formulations of the PU/KF biocomposite foam is tabulated in Table 1.

Table 1: Formulations of PU/KF biocomposite foam at different KF loadings

| Sample code | p-MDI (g) | PO-p (g) | Distilled water (pphp) ^a | Surfactant (pphp) ^a | Fibre loading (pphp) ^a |
|-------------|-----------|----------|-------------------------------------|--------------------------------|-----------------------------------|
| Control PU | 50.0 | 50.0 | 1.5 | 2.0 | - |
| SF1 | 50.0 | 50.0 | 1.5 | 2.0 | 2.5 |
| SF2 | 50.0 | 50.0 | 1.5 | 2.0 | 5.0 |
| SF3 | 50.0 | 50.0 | 1.5 | 2.0 | 7.5 |
| SF4 | 50.0 | 50.0 | 1.5 | 2.0 | 10.0 |
| SF5 | 50.0 | 50.0 | 1.5 | 2.0 | 12.5 |

^a part per hundred polyols

2.3 Characterisations of Rigid PU/KF Biocomposite Foam

2.3.1 Fourier Transform Infra-Red Analysis

Fourier Transform Infra-Red analysis using a Perkin Elmer 1000 model was carried out to identify the characteristic groups of PU such as urethane linkages and carbonyl groups. A small amount of sample was ground with KBr powder and pressed into a thin disc. Sixteen scans were averaged for each sample in the range of 700 cm^{-1} to 4,200 cm^{-1} .

2.3.2 Thermal properties of PU/KF Biocomposite Foam

Thermal gravimetry analysis (Perkin Elmer TGA7) was conducted to analyse the thermal degradation of the PU/KF biocomposite foam. The weight losses of the sample against temperature were recorded. Approximately 5 g of the sample was placed in the platinum pan and heated from 30 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$, under a nitrogen gas flow at 100 mL/min.

2.3.3 Compressive strength of PU/KF Biocomposite Foam

The compressive strength of the PU/KF foam was evaluated by a Universal Testing Machine Instron D100X. Sample with a dimension of 50x50x30 mm was prepared, and the test was conducted according to ASTM D1261. The crosshead speed of 5 mm/min was applied. The data of compression load and displacement were calculated at a rate of 10 points/s. The average of five readings for each formulation was reported.

3. Results and discussion

3.1 Fourier Transform Infra-Red Analysis

The FTIR spectra of PU biocomposite foam at various fibre loading is illustrated in Figure 1. The broad peaks at $3,310\text{ cm}^{-1}$ and $3,500\text{ cm}^{-1}$ corresponded to OH and NH stretching. By increasing the fibre loading, the peaks were becoming narrow and shifted to the right, which indicated the formation of hydrogen bonding between OH and NH groups. The detection of outstanding peaks at $2,922\text{ cm}^{-1}$ and $2,852\text{ cm}^{-1}$ were due to the asymmetric and symmetric stretching bonding of CH_2 of the PO-p (Alis et al., 2019). Meanwhile, the peak at $2,278\text{ cm}^{-1}$ was attributed to the vibrations of the remaining isocyanate NCO groups in the system (Dzulkipli et al., 2014). The band at $\sim 1,710\text{ cm}^{-1}$ was assigned to the existence of the C=O bond. Meanwhile, the bands at $1,533\text{ cm}^{-1}$, $1,530\text{ cm}^{-1}$ and $1,510\text{ cm}^{-1}$ were ascribed to the vibrations of urethane NH bending and CN stretching, that proved the formation of urethane linkages in the system (Nik Pauzi et al., 2014). Based on the spectra, all the common peaks of PU foam have been identified.

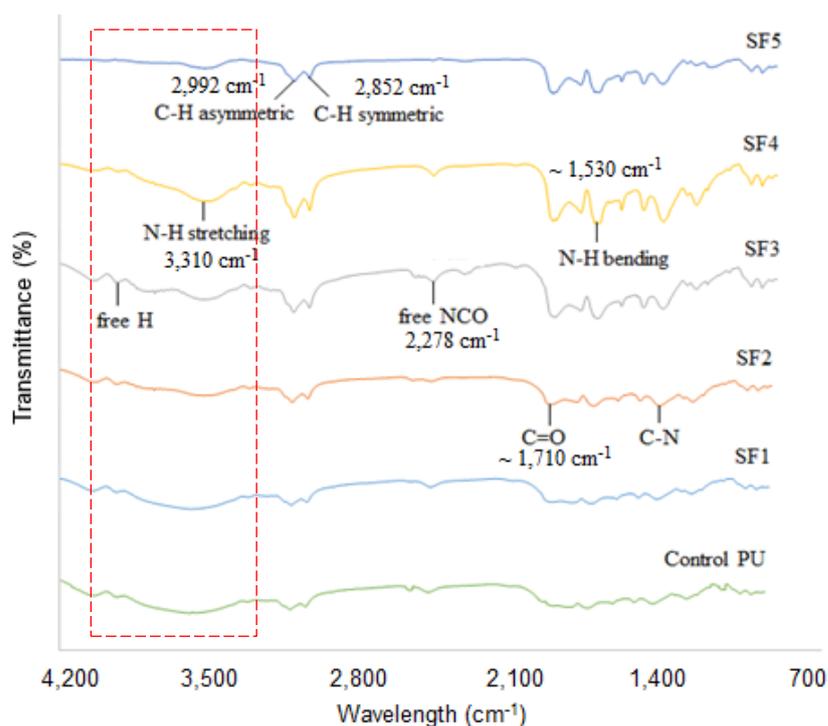


Figure 1: FTIR spectra of neat PU and PU/KF foams at various KF loadings

3.2 Thermal properties of PU/KF Biocomposite Foam

Figure 2 portrays the PU/KF biocomposite foam thermal properties at different KF loadings. A noticeable weight loss occurred at a temperature below $100\text{ }^{\circ}\text{C}$ usually due to the evaporation of water or moisture content in the fibre (Russo et al., 2013) and some small molecules (Jiao et al., 2013). The previous study showed that thermal degradation of PO-p based PU foam consists of three degradation regions (Nik Pauzi et al., 2014). As expected, the same behaviours were observed for all samples as shown in Figure 2.

The first region is related to the dissociation of the urethane bond (Czlonka et al., 2019) and the decomposition of some constituent of the natural fibres (El-Shekeil et al., 2012). The second region ($275\text{--}355\text{ }^{\circ}\text{C}$) corresponded to the decomposition of the soft segment polyols (Czlonka et al., 2019). Meanwhile, the cellulose of KF was degraded at $325\text{ }^{\circ}\text{C}$, which is comparable to the value reported in literature i.e. at $350\text{ }^{\circ}\text{C}$

(El-Shekeil et al., 2012). This is also proven by the significant weight loss of the SF5 in the second region, which contained the highest fibre loading. Meanwhile, the third region (420–450 °C) is correlated to the degradation of the high molecular weight of polyol. In this case, the formation of the hydrogen bonding between fibre-fibre and fibre-PU matrix is assumed to enhance the thermal stability of the biocomposite foam. From Figure 2b, SF5 exhibited better thermal stability, especially in the third region. It is reported that at higher fibre content, the agglomeration of the fibres tends to occur and consequently reduces the rate of heat transfer through the system (Banik and Sain, 2008). Apart from that, it is also thought that higher fibre content would increase the formation of the hydrogen bonding, thus improving the thermal stability of the biocomposite foam.

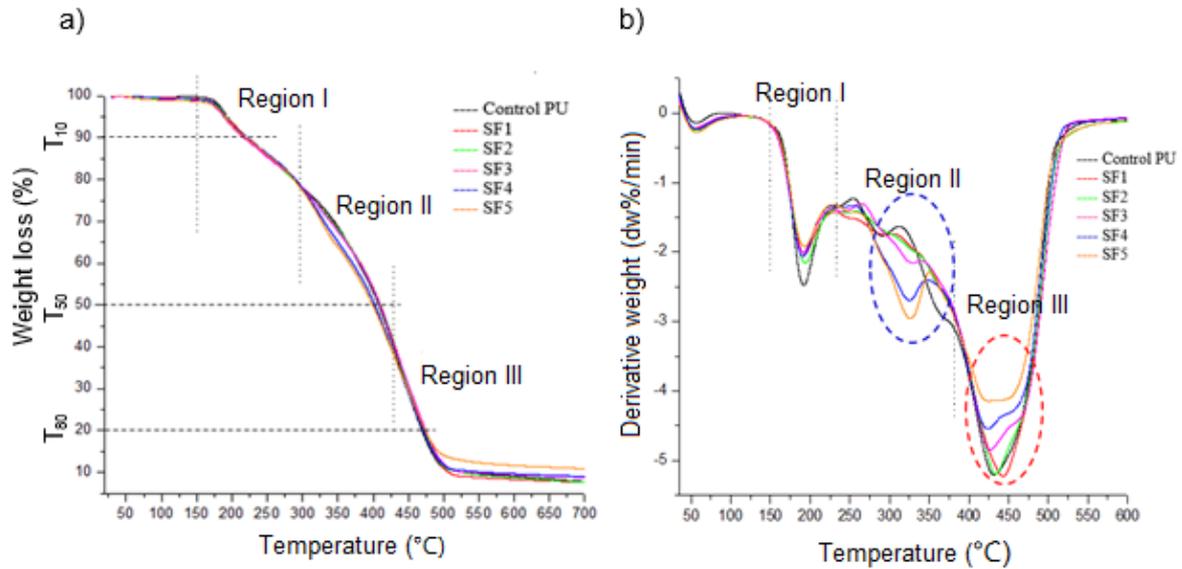


Figure 2: Thermal gravimetry analysis plot at different KF loadings; (a) Weight loss (wt%) against temperature profile and (b) Derivative weight loss profile of PU/KF biocomposite foam

3.3 Compressive strength of PU/KF Biocomposite Foam

Figure 3 shows the compressive strength of biocomposite foam against the KF loadings at 2.5, 5.0, 7.5, 10.0 and 12.5 pphp.

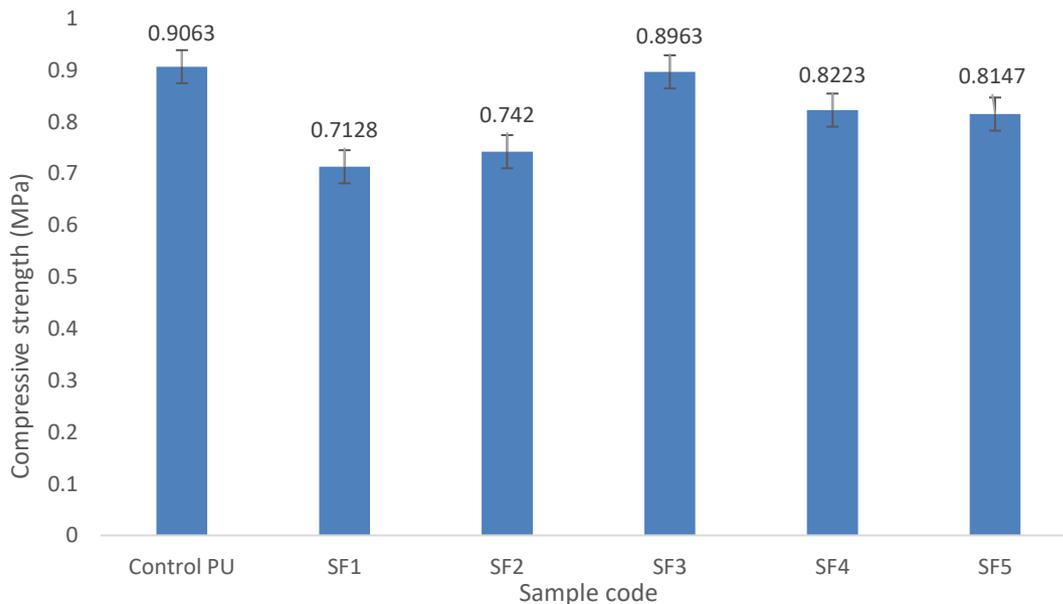


Figure 3: Compressive strength of PU/KF biocomposite foam at different fibre loadings

Overall, the addition of KF had reduced the compressive strength of the foams. The effect was noticeable at lower KF loadings when compared to the compressive strength of the control PU foam. At 2.5 pphp KF, the compressive strength of PU/KF foam was reduced almost 21 %, but it lessened to 18 % at 5 pphp KF. Further increased the KF loadings showed less significant effect on the compressive strength.

Sample SF3 (7.5 pphp KF) showed about 1.1 % reduction while samples SF4 (10 pphp KF) and SF5 (12.5 pphp KF) exhibited about 9.3 % and 10.1 % reductions. Obviously, these percentages were lower than that of samples SF1 and SF2. This can be postulated as follows; control PU foam has readily intra-hydrogen bonding that formed between urethane (-RNHCO) and hydroxyl (-OH) groups of PU chain. When KF was added, new inter-hydrogen bonding was formed between PU chains and -OH of KF. The presence of inter (weak) and intra (strong) bonding had negatively reduced the compression strength of PU/KF foam. By increasing the KF loadings, indirectly had increased the amount of -OH in foam. This induced the formation of intra-hydrogen bonds in KF, thus forming KF-rich regions (i.e. agglomeration). The agglomeration of the KF caused the discontinuity in the PU matrix and subsequently created more stress concentration point in the foam (Badri et al., 2005).

According to Czlonka et al. (2019), high filler content might also cause a non-uniform dispersion of filler-polyol mixture in the matrix. This would lead to the formation of the discontinuous domain due to the agglomeration of the filler and weakened the interfacial adhesion between the filler and active reaction site. As a result, the compressive strength of the foam was reduced. Since the amount of KF was small, the agglomeration effect could not surpass the strength of hydrogen bonding in the PU chain. These observations were manifested by samples SF3, SF4 and SF5, which showed small percentages of reductions when compared to the control PU foam.

A similar trend was also reported by Nar et al. (2015), where the addition of higher filler content showed a negative reinforcement impact on compressive strength. The presence of KF-rich region had also explained the increase of thermal stability in samples SF3, SF4 and SF5 where extra heats were needed to break the intra-hydrogen bonds (agglomerated KF-rich region) in the samples. The agglomeration had also decelerated the heat transfer across the foams, thus increasing their thermal stabilities.

4. Conclusion

A rigid polyurethane biocomposite foam based on PO-p and 2.5, 5.0, 7.5, 10.0 and 12.5 pphp of KF was successfully prepared via direct mixing method. The FTIR analysis confirmed the formation of PU/KF biocomposite foam based on the detection of common polyurethane functional groups. The PU/KF biocomposite foams exhibited better thermal stabilities compared to that of control PU foam. The formation of intra-hydrogen bonding in KF-rich region had increased the thermal stabilities of the foams since more heat was needed to break the bonds. Nevertheless, the presence of KF-rich region had led to KF agglomeration, which created stress concentration in the foam, thus reducing the compressive strength. However, sample with 7.5 pphp KF showed a less significant reduction (at about 1.1 %) with respect to that of control PU. Since the amount of KF was small, the agglomeration effect could not surpass the strength of hydrogen bonding in the PU chain, thus the percentage of reduction was small.

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